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A Study of the Relative Reactivity of Carbon From Coal Using the Bouduard Reaction

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A STUDY OF THE RELATIVE REACTIVITY OF CARBON FROM COAL USING THE BOUDUARD REACTION

by
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This thesis submitted by Jay Robert Kauphusman in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

Chars made from two lignites, a subbituminous coal and a bituminous coal, were reacted with CO_2 over a range of temperatures and space times to determine the effect of coal rank on the conversion of CO_2 to CO by the Bouduard reaction. The rank of the coals tested was found to have a definite effect on the conversion of CO_2 with the degree of conversion decreasing with increasing rank. Conversion increased with increasing temperature and contact time. Calculation of the heats of formation of the carbon constituents of these coals from the pseudo equilibrium data indicate that the carbon in the lower rank coals is in a more reactive state.

The effects of sodium concentration of the coals on the conversion of CO_2 were also studied. Analysis of variance for a two way classification design indicate that the sodium content of the coals is significant. The number of experiments of this type was too small to predict a definite trend in the relationship of conversion to sodium content, but evidence indicates that increased sodium concentration increases conversion.

INTRODUCTION

Greater industrialization and mobilization, as well as population growth, have increased the demand for energy in the United States. In the years 1900-1955 the total energy consumption of the United States increased over fourfold or at an average annual rate of 3.1 percent (1). The total energy consumption in 1955 amounted to 40,796 trillion Btu, equivalent to 1,557 million tons of bituminous coal with a heating value of 26.2 million Btu per ton. By 1970 energy consumption was 69,000 trillion Btu or 1.69 times the 1955 total. Per capita consumption of energy in 1970 was 338 million Btu per year, equivalent to 6.7 gallons of petroleum per day. Projections of energy use from 1970 to 2000 predict an increase in total energy demand by a factor of 2.5 to 3 (2).

As technology has advanced, the sources of energy have become more sophisticated as evidenced by two changes in the country's energy base since 1850; first from wood to coal, then from coal to natural gas and oil (1). Today oil and natural gas supply approximately 75 percent of the energy requirements of the United States (3). The growth of the natural gas industry has been phenomenal. In the last 25 years, natural gas has been used for 50 percent of the nation's new energy requirements, but at present the projected demands are already greater than what proven reserves in the contiguous 48 states will be able to supply (4).

Two methods of meeting future natural gas requirements are importation of liquefied natural gas or manufacture of synthetic gas from coal. In view of possible restrictions on imports or a possible international crisis halting imports, coal gasification will probably provide an important source of gaseous fuels. The main advantage of coal gasification is the abundance of coal available in this country.

The technology of producing a low heating value gas from coal dates back to the early 1800's, but the use of this gas was limited mainly to the steel industries (5). Recently the Interior Department's Office of Coal Research has agreed to provide $30 million per year for 4 years to private firms in an effort to stimulate progress towards the development of a commercially acceptable process for manufacturing a high heating value gas from coal (4).

At present there are several processes under development for producing high heating value gas. These include the Bigas process developed by Bituminous Coal Research, Inc., the Hygas-Oxygen process developed by the Institute of Gas Technology, the Steam-Iron process developed by IGT - Fuel Gas Associates and the Synthane process developed by the U.S. Bureau of Mines (3). These processes all have several features in common; the reaction of coal with oxygen or air and steam in a gas producer to form a synthesis gas and the methanation of this synthesis gas to a high-heating-value pipeline gas.

The synthesis gas for the methanation step consists primarily of H_2 and CO, and is usually the result of several simultaneous reactions involving CO_2, CO, H_2, O_2 and H_2O. A primary reaction is:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} - 174{,}600 \text{ Btu/lb mole C}$$

This reaction provides thermal energy for the following endothermic reactions:

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)} + 70{,}200 \text{ Btu/lb mole}$$

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)} + 70{,}900 \text{ Btu/lb mole}$$

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} + 700 \text{ Btu/lb mole}$$

It is desirable to have a H_2/CO ratio of about 3:1 in the gases from these reactions if methane is to be synthesized. The synthesis gas is purified and then methanated over a nickel or iron catalyst:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} - 88{,}000 \text{ Btu/lb mole}$$

Because all coals can be gasified and because the production of CO is so important in the gasification processes, the primary objective of this investigation is to determine if there is a relationship between the rank of coal and the reactivity of the constituent carbon towards CO_2 in forming CO as in reaction 2. The reactivity of the carbon is defined as the rate of CO formation by the coal substance at defined temperature, pressure and flow conditions (6).

The results of these reactivity investigations may provide useful information for determining a set of criteria for use in selecting coals for gasification processes, and may prove to be of some value in determining uses for coals which cannot be mined either for economic or ecological reasons. Such coals may be gasified underground to produce a gas for synthesis of a high-heating-value pipeline gas or for its heating value.

If of high reactivity, the large deposits of low-rank coals in the Northern Great Plains Province, about 45 percent of the nation's solid fuel reserves, would become even more important in the total energy picture to meet expanded energy needs.

LITERATURE REVIEW

There is a substantial amount of information available on the production of producer gas as such, but very little information was found pertaining only to the Bouduard reaction. As this reaction was of primary interest, references pertaining to the Bouduard reaction were particularly useful.

Clement, Adams and Haskins (7) examined the effects of temperature and gas flow rate on the production of CO by the Bouduard reaction. Their experiments were performed by passing a stream of CO_2 through a bed of fuel contained in a porcelain tube heated by an electric furnace. The CO_2 was supplied by a tank of liquid CO_2. By metering the flow of gases from the reactor, they were able to calculate the contact time of the gases. The exit gases were analyzed by the Hempel method. From their experiments, they were able to plot the relationship of the percent CO formed and the temperature and contact time.

Professor C. N. Haskins used the data of Clement, et al., for approximating the constants k_1 and k_2 in the rate equation for the Bouduard reaction with respect to CO:

$$\frac{d(CO)}{dt} = k_1 (CO_2) - k_2 (CO)^2$$

Wenzel, Meraikib and Franke (6) investigated the effect of alkaline carbonates on the reactivities of coals and measured the reactivity with regard to the Bouduard reaction using parameter, k_m, the rate constant for the equation:

$$-\frac{dNc}{dt} = -\frac{dN\ CO_2}{dt} = k_m \times M_c\ [(CO_2) - (CO_2 - G_1)]$$

where M_c is the availability of carbon, (CO_2) is the concentration of CO_2 in the exit gas and (CO_2-G_1) is the thermodynamically required equilibrium concentration. The temperature dependence of the rate constant was determined by the Arrhenius equation. The experiments were performed by passing CO_2 into a heated tubular reactor which contained the carbonates and char or coke. The results showed that the addition of carbonates does have an activating effect. They also found that the coals affected the least are those which are naturally reactive while those affected the most are those that are naturally the least reactive.

In another investigation by Franke and Meraikib with Nefedow (8), the influence of metal vapors on the reactivities of coals was studied. Here again the Bouduard reaction was the reaction under study and the rate constant, k_m, was the measure of reactivity. The results were mixed and inconclusive. A trend, however, was that there was a reactivity increase due to the presence of the metal vapors at the lower temperatures (800° C) studied and an inhibiting effect noted at the higher temperatures (1100° C).

G. C. Scott and G. W. Jones (9) investigated the effect of time of contact on the concentration of effluent gases from the oxidation of anthracite in an effort to establish a means of predicting the trend of a mine fire by sampling the effluent gases from the burning area. The results were such that they concluded that the percentage of oxygen in the gases was of little value of predicting the activity of the fire.

Though this report contained no information on the Bouduard reaction, there was a description of their apparatus, which could be adapted for use in this investigation and a method for calculating the time of contact of

the gases. This information proved quite useful in determining the experimental methods used in this investigation. The work of Clement, Adams and Haskins (7) was used to the greatest extent as a reference because their methods adapted themselves well to a study of the rate of formation of CO.

The coals studied by Franke, et al (6, 8) were European brown coal, gas coal and bituminous coal. Clement, Adams and Haskins performed their experiments with charcoal, coke and anthracite. There was no information available on the reactivity of lignite and subbituminous coals from the United States.

SCOPE OF INVESTIGATION

The objectives were to determine the effects of rank and of sodium content on the reactivity of coal measured by conversion according to the Bouduard reaction:

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)} + 70{,}200 \text{ Btu/lb mole}$$

This reaction was chosen because of its importance as a major reaction in the formation of synthesis gas that may be used in producing a high-heating-value pipeline gas.

Standardized conditions of temperature, pressure and gas feed are necessary for comparing reactivities. Each coal was tested at three temperature levels of 1100°, 1250° and 1400° F, and at four space times of 5, 10, 25, and 50 seconds. These space times are determined by the flow into the reactor. All experiments were carried out at atmospheric pressure.

The coals tested included a bituminous coal, a subbituminous coal and two lignites. The coals were carbonized simultaneously in a slot oven to drive off some volatile matter, and were then crushed and screened to the desired size fraction of 16 by 30 mesh. The experiments were performed in an externally-heated flow-through reactor containing a fixed bed of the test coal. Each sample was gasified at the same temperatures and space times; in this manner it was possible to gather data for comparison of reactivities.

The reactivity was measured by the percentages of CO present in the exit gas. Results of these experiments were compiled and analyzed statistically to determine if significant differences in reactivity existed.

Experiments were also performed on the two lignite coals to determine if the sodium concentration, reported as percent sodium oxide in the ash, had any significant effect on the reactivity. These experiments were performed in the same manner except the sodium concentrations were increased or decreased by adding sodium or by leaching the chars with acid solutions.

EXPERIMENTAL DESIGN

As in most experimental situations there was more than one factor affecting the outcome of the experiments. The independent variables of temperature, space time and type of coal are considered to influence the formation of CO. In order that the significance of these variables may be determined, an experimental design suitable for statistical analysis was used. The variables of coal, temperature and space time were considered in one experimental design, and the variables of sodium concentration and contact time in another.

The four coals are taken to be fixed effects while the three temperatures and four space times are considered to be random effects representing a range of possible space times and temperatures. These variable levels were combined into a mixed model 3 x 4 x 4 factorial design for analysis of variance to determine the possible significance of differences due to these variables.

The variables of sodium concentration and space time were combined into a random-model two-way classification design. Both the contact time and sodium concentration were considered to be random effects. Explanations of these designs and analyses are available in Volk (10) and Wine (11).

The significance level selected was 0.05, which means that there was a 0.05 probability of falsely rejecting the null hypothesis.

Of major interest is the null hypothesis that the effects of the coals on the conversion of CO_2 to CO were all equal to zero. Letting factor B represent the coal effects, this null hypothesis can be written:

$$H_{OB} ; B_1 = B_2 = B_3 = B_4 = 0 \quad (11).$$

Letting factor A represent the temperature effects and factor C the space time effects, the other null hypotheses are written:

$$H_{OA} ; A_1 = A_2 = A_3 = 0$$

$$H_{OC} ; C_1 = C_2 = C_3 = C_4 = 0$$

The model equation for the design including the three factors and their interactions is written:

$$X_{ijku} = U + A_i + B_j + C_k + (AB)_{ij} + (AC)_{ik} + (BC)_{jk} + E_{ijku}$$

For the second design the appropriate model equation is:

$$X_{ij} = U + A_i + B_j + E_{ij}$$

The null hypotheses are similar to those of the first design.

MATERIALS TESTED

Coals

The bituminous coal (A) was obtained from Consolidation Coal Company's Arkwright mine at Osage, West Virginia, and the subbituminous coal (C) from Western Energy Company's mine at Colstrip, Montana. The North Dakota lignites were from the Larson pit of Baukol-Noonan, Inc. (B), and the Gascoyne mine of the Knife River Coal Mining Company (D). As indicated, these coals will be designated A, B, C and D for simplifying future references (see Appendix A, Table 1). The analyses of coals and their ash on an as-received basis are given in Appendix A, Tables 2 and 3.

Sample Preparations

As received, the coals contained volatile matter which would be released on heating in the reactor. The released gases would consist primarily of hydrogen and methane with some CO_2, CO and tar vapors included, and would influence the results of the reactivity measurements because of the dilution effect on the gasifying medium.

The volatile matter content was reduced by carbonization. A 50-pound sample of each coal was placed in an iron retort, and the retorts were placed in a slot oven at 1100° F. The samples were maintained at this temperature for approximately 7 hours. Coals B, C and D formed unconsolidated chars while coal A formed a hard porous coke.

The proximate analyses of the carbonized samples are given in Appendix A, Table 4. After carbonization the samples were sized by crushing and screening. The particle size range used was 16-30 mesh (0.59 - 1.19 mm), similar to the size used by Scott and Jones (9). Carbonization and sizing were the only preparations required.

Two samples of char D having sodium concentrations greater than the original char were prepared by spraying water solutions of sodium acetate on the samples followed by redrying. Char B originally had a high sodium concentration in its ash, and attempts were made to leach sodium from the char by treatment with strong acid solutions to reduce the sodium concentration. This process replaces the sodium with hydrogen by ion exchange. An effort was made to obtain samples in a wide range of sodium concentration, but analyses showed that all the extracted samples contained from 14 to 17 percent sodium oxide in their ash, indicating that there may be a limiting value as to the amount of exchangeable sodium in a given char. The ash analyses of chars B and D and the samples prepared from them are given in Appendix A, Tables 5 and 6.

CO_2 Source

The CO_2 source was a 50-pound cylinder of commercial grade CO_2. The minimum purity for the commercial grade specifies 99.5 percent.

EQUIPMENT

The principle equipment used for investigating the Bouduard reaction included a reactor, a furnace to provide the heat for and maintain the reaction temperature and a system for delivering and metering the flow of CO_2 into the reactor. The percentages of CO and CO_2 in the exit gas were determined by sampling and analyzing the gases with an Orsat apparatus. The schematic flow diagram is shown in Figure 1.

Reactor and Furnace

A tubular reactor in which a fixed bed of char rested on a porous support has been used successfully in similar work (6, 7, 8, 9), and the same concept was employed in this investigation. The final design of the reactor is shown in Figure 2.

The reactor was designed for use with a Burrel model B-1-23 tube furnace capable of maintaining temperatures up to 2300° F. The heating zone of this furnace is 23 inches long and permits the use of a reactor up to 2 inches in outside diameter. An effort was made to design the reactor so that the bed of char would be centered in the heating zone of the furnace.

The temperature of the furnace was controlled and recorded by a Honeywell Electr-O-Pulse relay controller used in conjunction with a strip chart recorder. The temperature sensor was a shielded chromel-alumel thermocouple.

The reactor was fabricated of 2 inch nominal outside diameter schedule 40 type-304 stainless steel pipe. Stainless steel was

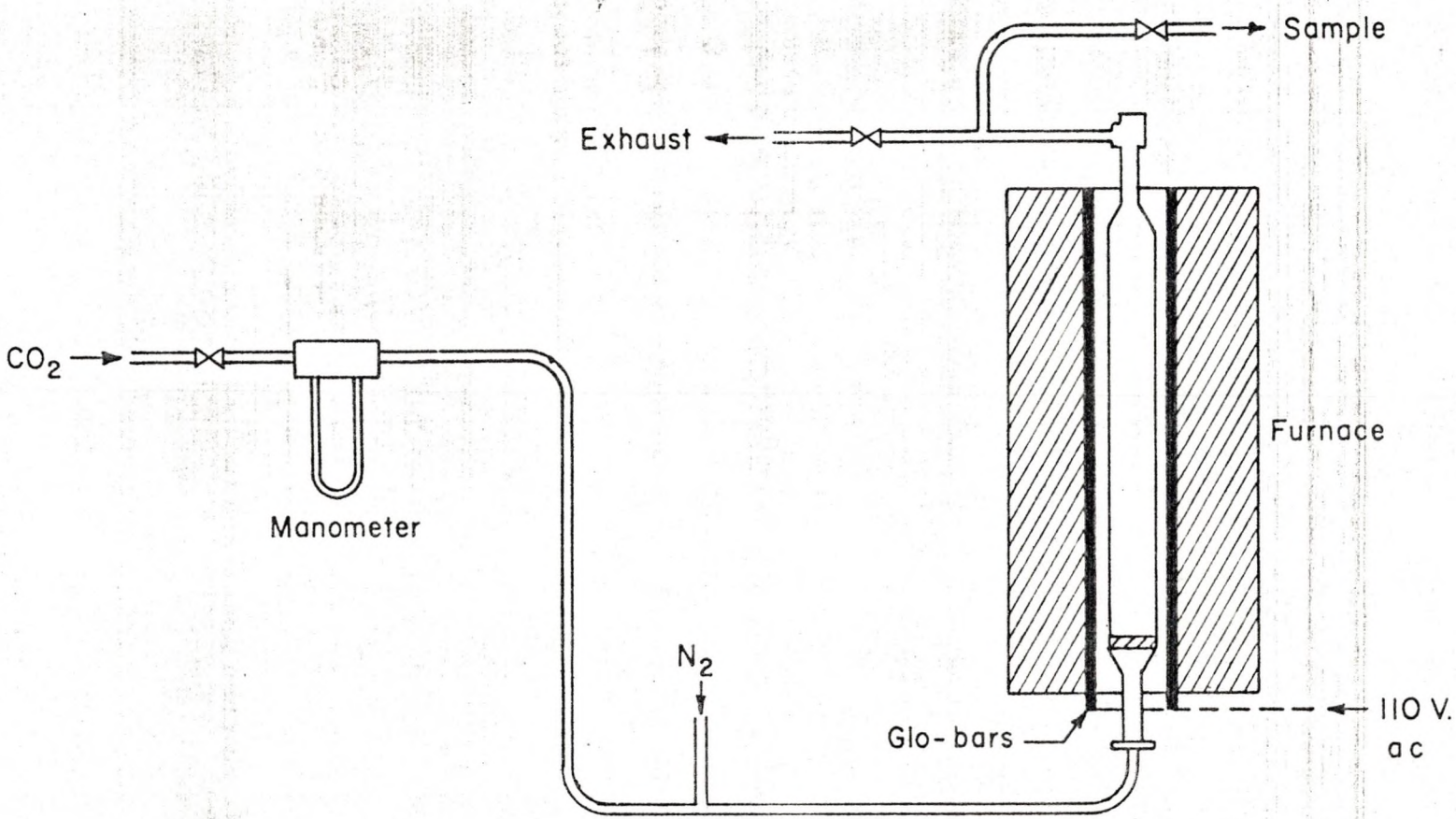

Fig. 1-- Schematic diagram of equipment.

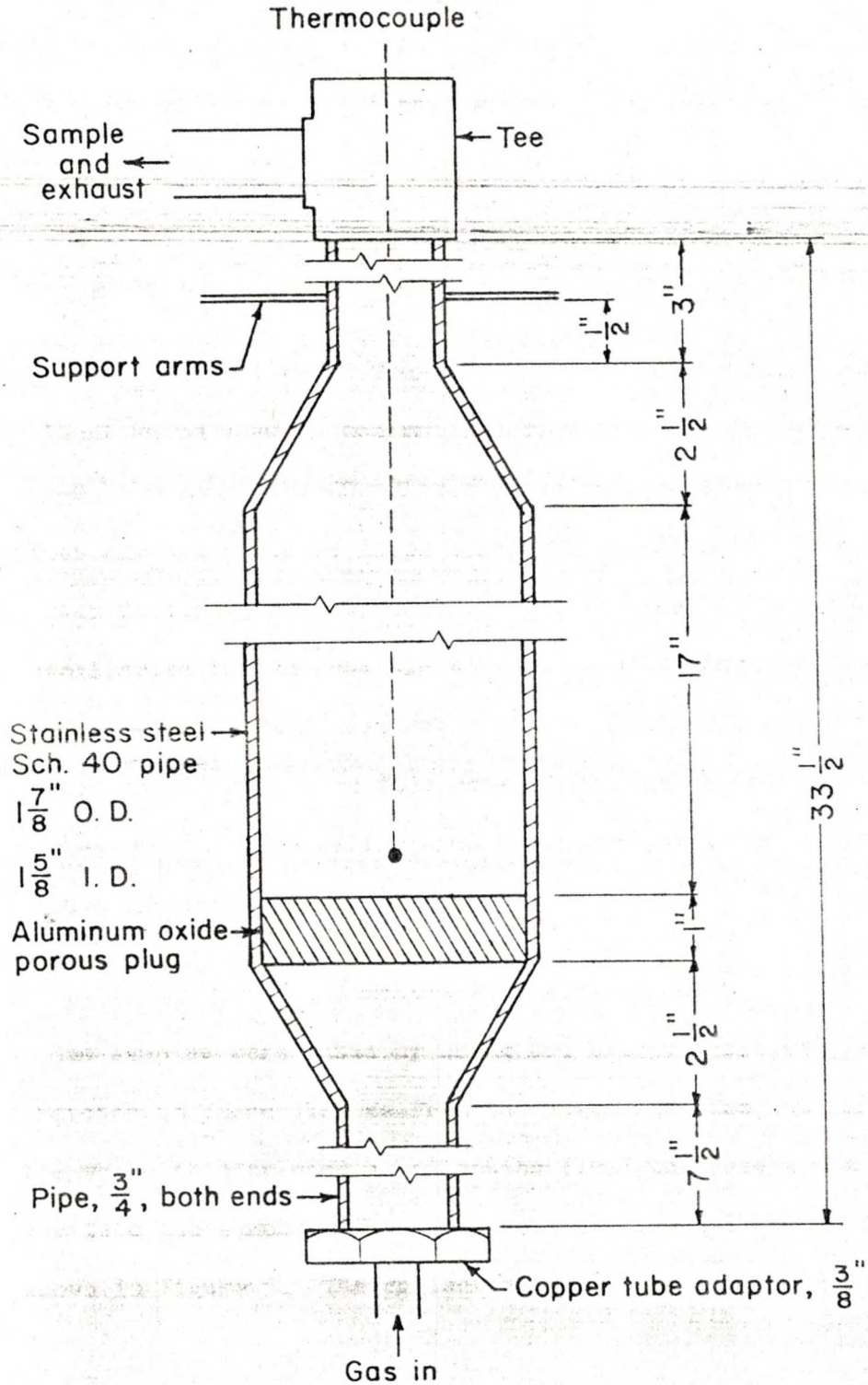

Fig. 2 -- Cross section of reaction tube.

chosen because of resistance to scaling under repeated heating and cooling and brittling by the carburizing conditions to which it would be exposed.

The reaction tube was fitted with a porous plug of alumina. The purpose of this plug was to support the bed of char and to uniformly distribute the CO_2 entering the reactor.

CO_2 Flow Meter

The CO_2 was delivered from a cylinder with a regulator and an additional valve used to control the flow. An orifice type meter was employed to measure the CO_2 flow. Glass capillaries were used as orifices and the pressure drops across the capillaries were read on a manometer filled with unity oil. By varying the length or diameter of the capillaries it was possible to cover a wide range of flow rates. Each capillary was calibrated against a standard wet test meter to determine the relationship of volume flow rate of CO_2 and the manometer readings in inches of oil. The calibration curves prepared for the flow meters are shown in Figures 3 and 4.

Sampling Apparatus

Gas samples were taken by using the slight positive pressure in the reactor to force the gas from the discharge line into a sampling bottle where it displaced a collecting fluid to prevent the seepage of air into the sample. The apparatus used for collecting the samples is shown in Figure 5. The collecting fluid was a solution of water,

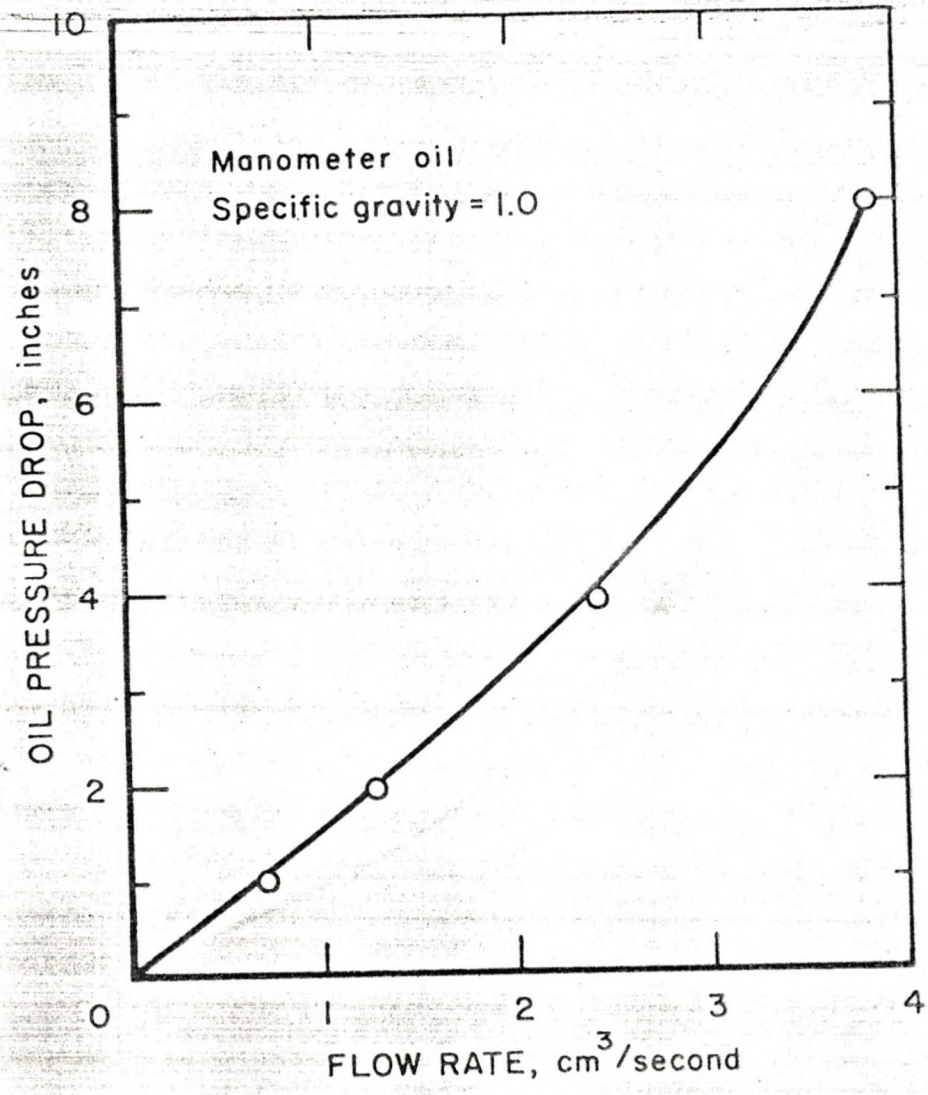

Fig. 3 -- CO_2 flowmeter calibration. 0 to 4 cm^3/sec.

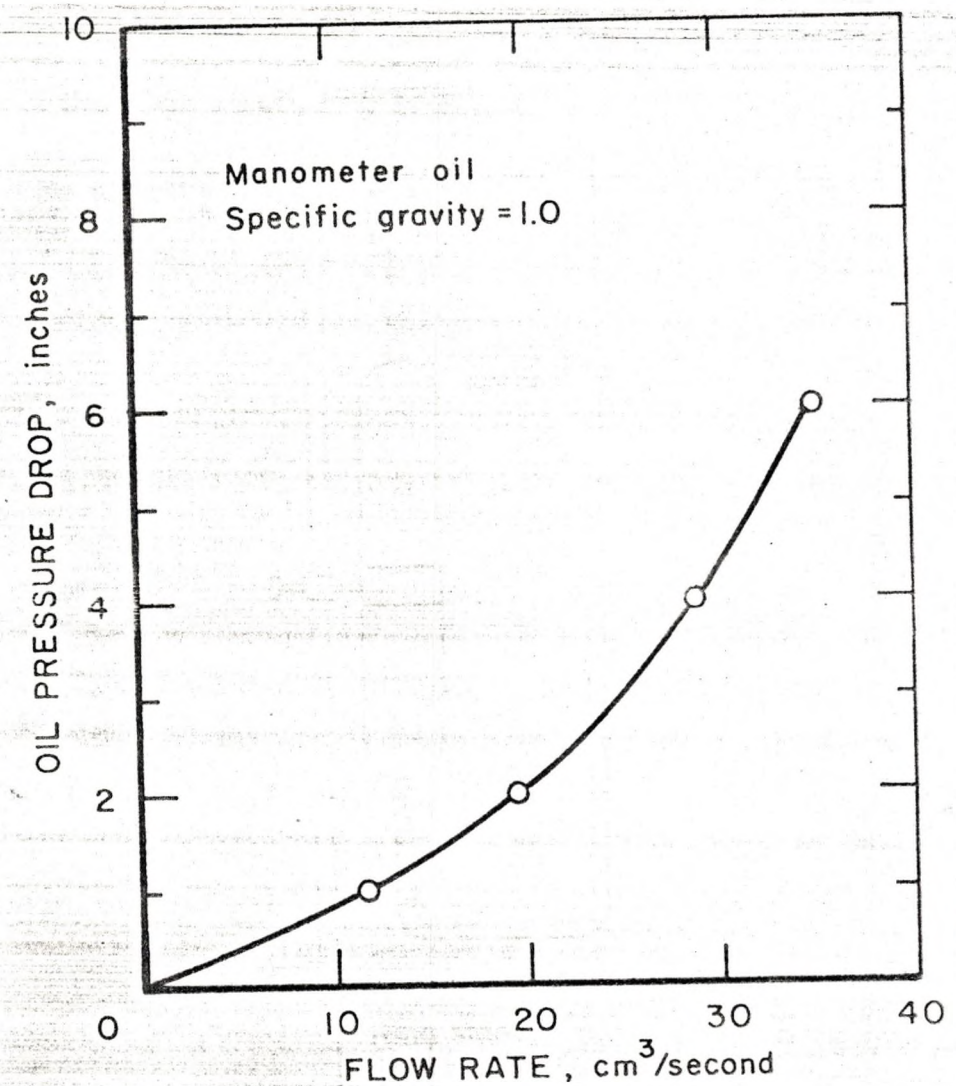

Fig. 4--CO_2 flowmeter calibration. 0 to 40 cm^3/sec.

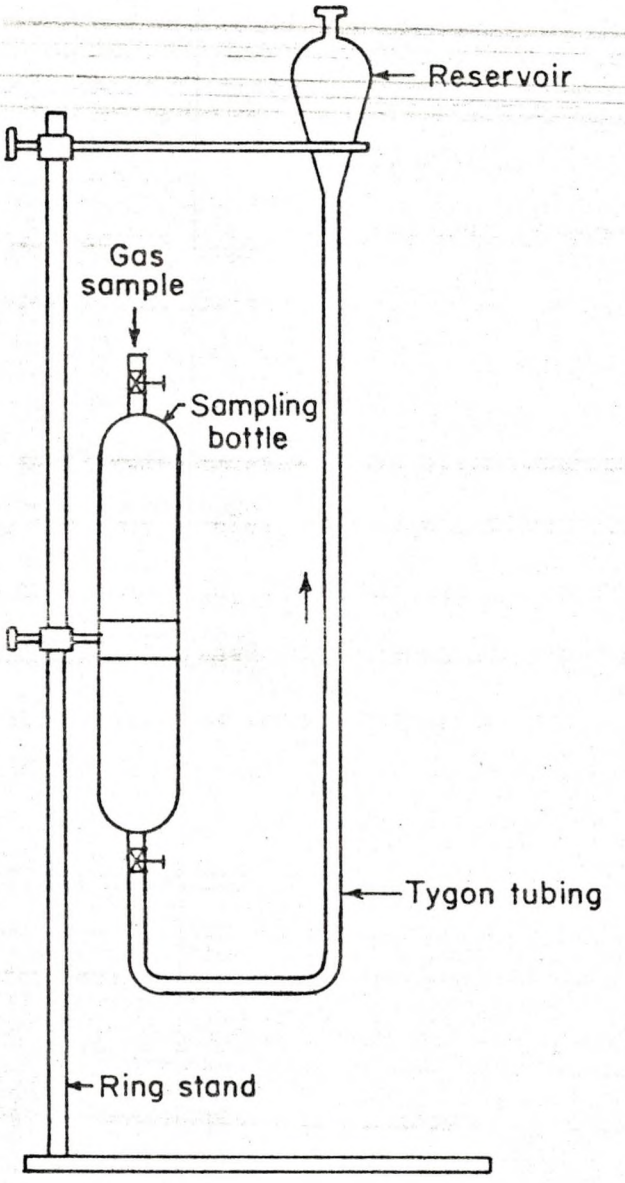

Fig. 5 -- Sampling apparatus.

sulfuric acid and sodium sulfate. The low solubility of CO_2 in the acid solution reduced errors in the gas analysis due to absorption of CO_2.

Orsat Apparatus

A standard Orsat apparatus with a burette calibrated from zero to 100 milliliters was used to analyze the gas samples for CO and CO_2. The CO_2 was absorbed in a contact pipette filled with a potassium hydroxide solution and the CO was absorbed in a bubbler pipette filled with an acidic cuprous chloride solution.

Gas Chromatograph

A Burrel model K-3 Kromo-Tog gas-liquid chromatograph was available for use in analyzing the gas samples. The separation columns did not permit the analysis for CO and CO_2 simultaneously. The chromatograph, using a silica gel column, was used for determining the time necessary to remove the remaining volatiles from the samples.

PROCEDURES

Sample Measuring and Charging

It was necessary to insure that the same volume of char was placed in the reactor for each experiment because the space time is dependent on the void volume of the reactor. A piece of 2 inch schedule 40 pipe was cut to a length of 30 centimeters, the same as the bed depth desired, and one end was closed with a flat plate. By filling the pipe and leveling the top, the correct volume of char could be measured. The weights of the samples were recorded for each experiment and are given in Appendix A, Table 7.

The thermocouple was placed in the reactor with the hot junction resting on the porous plug. The sample of char was then poured around the thermocouple without tamping. The thermocouple was then raised 1 inch from the plug and the fittings holding the thermocouple were tightened to seal the reactor.

Preheating

The electric furnace, temperature recorder and temperature controller were switched on and nitrogen was passed through the reactor. The furnace was maintained at the reaction temperature for approximately 16 hours prior to the start of a test. This heating period was necessary because the initial carbonization at 1100° F for 7 hours was insufficient to remove all volatile matter from the char. The nitrogen flow was used to flush released volatiles from the reactor.

The length of the initial heating period was determined by the time necessary to produce a gas sample which upon chromatographic analysis of a gas sample showed no methane peak and a very small hydrogen peak. After several tests it was determined that 16 hours was sufficient time to remove the volatile matter and the gas chromatograph was no longer used as an indicator.

After the heating period was complete, the nitrogen flow was stopped. The CO_2 flow was started at the rate necessary to give desired space time. The introduction of CO_2 lowered the temperature because of the thermal requirements of the reaction. Several minutes were required for the controller to adjust the reactor temperature to the desired level. During this stabilization period, essentially all of the purge nitrogen was flushed from the reactor.

Sampling Procedure

The valve on the exhaust line was closed and the valve on the sampling line opened. The sampling bottle was connected into this line for taking a sample; otherwise, the gas was exhausted. When the reactor temperature stabilized at the desired temperature level, the sampling process was begun. Samples were taken at intervals and analyzed for CO and CO_2 until the analyses were reasonably constant. At least three consistent analyses were obtained and recorded before terminating a test.

After the reaction had reached a steady state and the analyses had been recorded, the flow rate was changed to provide the next space

time. The order in which the flow rates were tested was varied in a random manner to prevent any bias in the statistical analyses. Several minutes were usually required for the reaction to return to a steady state after changing the flow rate. After some experience in operating the equipment was acquired, it became possible to judge the time required and a minimum number of samples was needed.

The sampling procedure was repeated for each contact time and the analyses were recorded. The Orsat apparatus was used to determine the volume percentages of CO_2 and CO. The total of these two gases represented more than 90 percent and usually more than 95 percent of the gas leaving the reactor.

The same procedures were followed in the experiments relating sodium concentration to reactivity.

RESULTS

The analyses of the gases were adjusted to a basis in which the total of CO and CO_2 represented 100 percent. This was done by the following method:

$$\text{Percent CO} = \frac{\text{volume CO/100 ml}}{\text{volume CO + } CO_2\text{/100 ml}} \times 100$$

This percentage of CO was calculated for each recorded analysis and the three most consistent percentages were averaged.

The results of the experiments relating reactivity to coal rank are given in Appendix B, Table 8. These results are shown for the space times based on the flow rate of CO_2 into the reactor. These same results are shown in Figures 6, 7 and 8, but with the residence times calculated from the volume of gas leaving the reactor. An explanation of the method used in calculating the residence times is given in Appendix C.

Effect of Coal Rank

The analyses of variance tests performed on the 3 x 4 x 4 factorial design confirm that there were significant differences in the reactivities of the coals as tested. The null hypothesis, which states that the effects of rank are all equal to zero, could not be accepted at the 0.05 significance level. The analysis of variance table for this design is shown in Appendix B, Table 11. An example of the calculations involved is given in Appendix C.

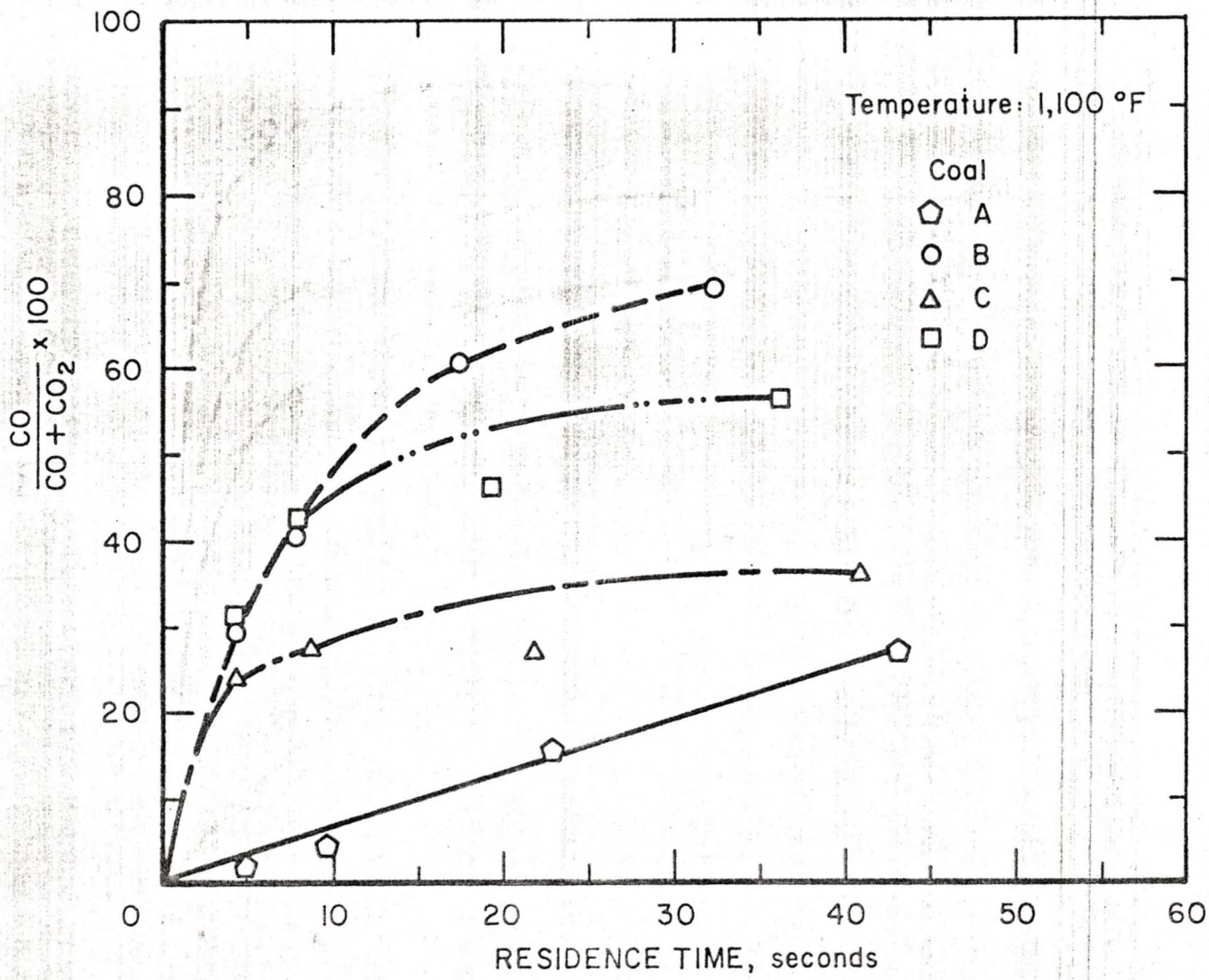

Fig. 6-- Percent CO vs residence time, results at 1,100 °F.

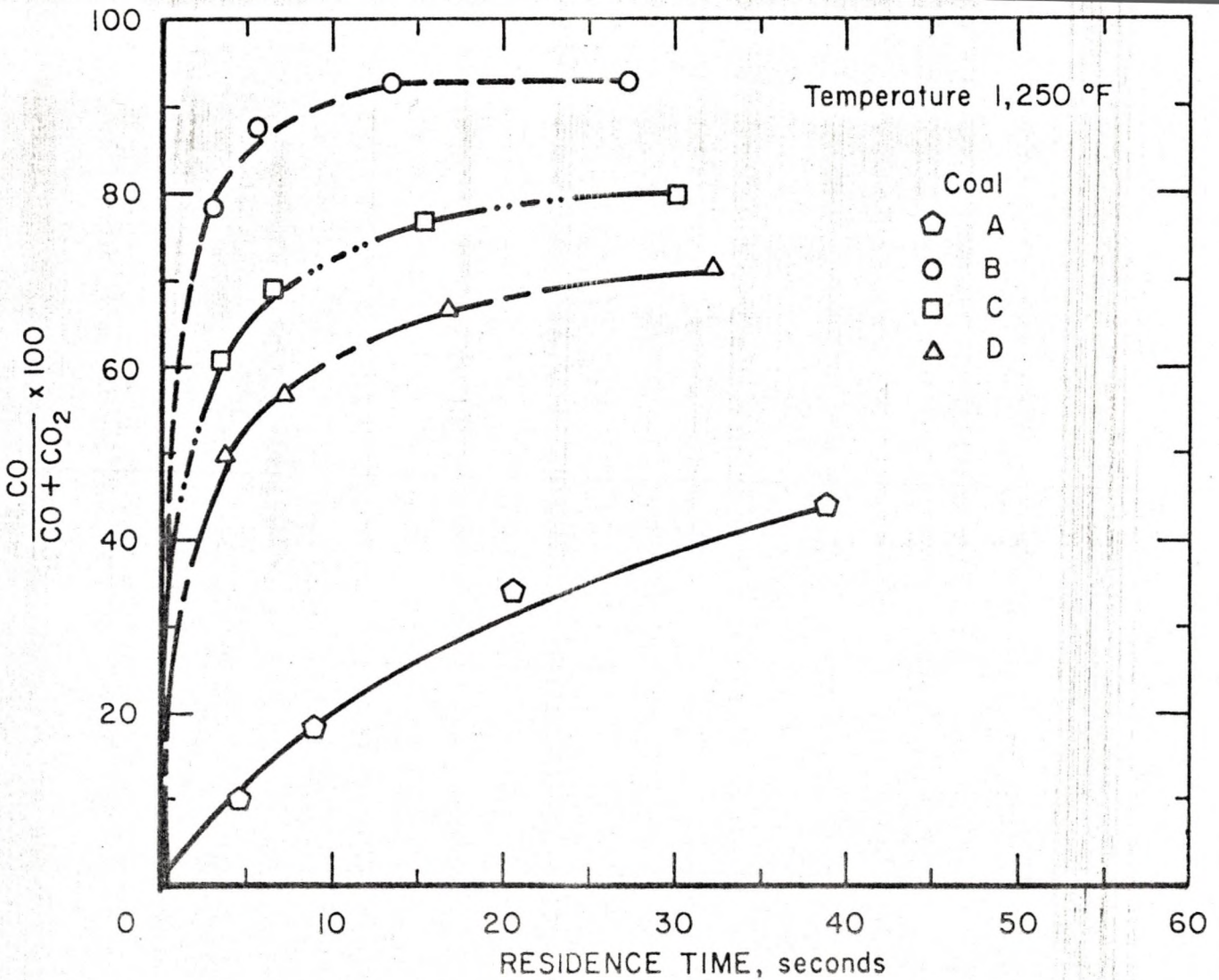

Fig. 7--Percent CO vs residence time, results at 1,250 °F.

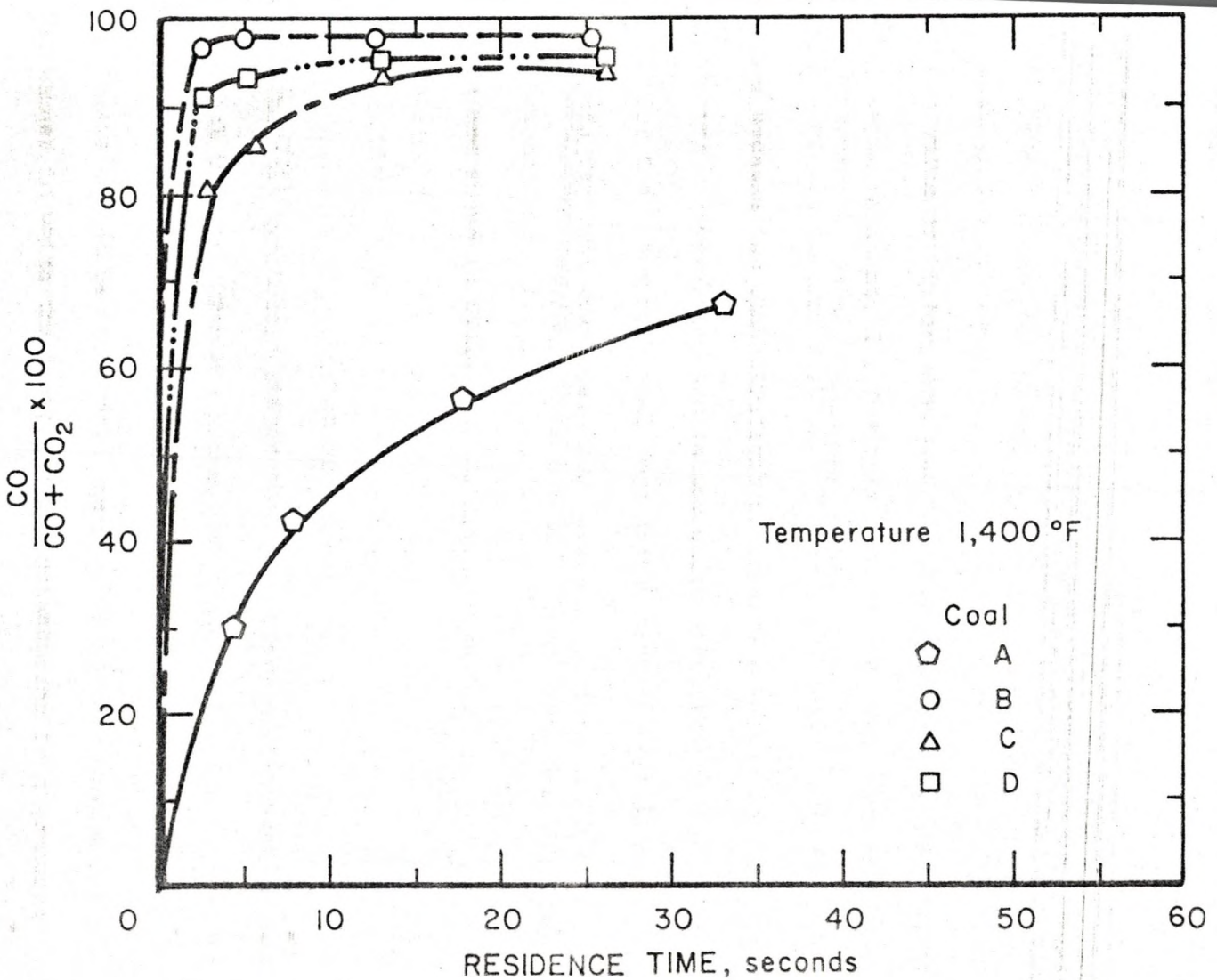

Fig. 8-- Percent CO vs residence time, results at 1,400 °F.

The order of reactivity of the samples from greatest to least was B, D, C and A. In terms of coal rank, the lignites were most reactive and the bituminous coal was least reactive. The same order of reactivity was noted at each of the three temperature levels investigated.

A comparison of conversions was made with that of beta graphite by calculating the equilibrium constant for the Bouduard reaction using established thermodynamic data for CO_2, CO and beta graphite. The highest value of CO for each test was then used to calculate a pseudo-equilibrium constant, K_p, for each char at each temperature. The K_p values calculated from test data do not represent true equilibrium values because the concentrations of CO were observed to be slowly increasing. However, of the values calculated from data, all but those for the bituminous coal were higher than the equilibrium constants for beta graphite. The values of K_p for the beta graphite reaction are shown in Table 10, and the values of K_p for the coals tested are shown in Table 11. Methods for calculation are given in Appendix C.

Effect of Temperature

The null hypothesis states that the effect of temperature are all equal to zero. Table 9 shows that the calculated F is greater than the critical F at the 0.05 significance label, so the null hypothesis cannot be accepted. The results of this test agree with the manner in which the equilibrium constants for beta graphite increase with temperature, meaning that the Bouduard reaction is highly temperature dependent.

Effect of Space Time

The percentage of CO in the product varied with the space time of the gasifying medium. The F test for the null hypothesis, that the effects of residence time are all equal to zero, was significant.

The effect of contact time becomes less as the temperature level is increased. The reaction velocities increased such that the reaction nears completion in a shorter time, as illustrated in the curves for coals B and D in Figure 6.

Effect of Sodium Concentration

The results of the experiments relating sodium concentration to reactivity are shown in Appendix B, Tables 13 and 14, and are plotted in Figures 9 and 10. The results of the analyses of variance tests in Table 15 show that the effects of adding sodium to char D were significant. Samples D-1 and D-2 were more reactive than char D, but D-2 with 6.5 percent sodium oxide in its ash was more reactive than D-1 with 8.4 percent sodium oxide in its ash.

The tests performed with samples of char B which had been leached in acid solutions indicated significant increases in reactivity, with reduced sodium content, as shown in Appendix B, Table 16. This is in direct conflict with the results obtained using char D, to which sodium had been added.

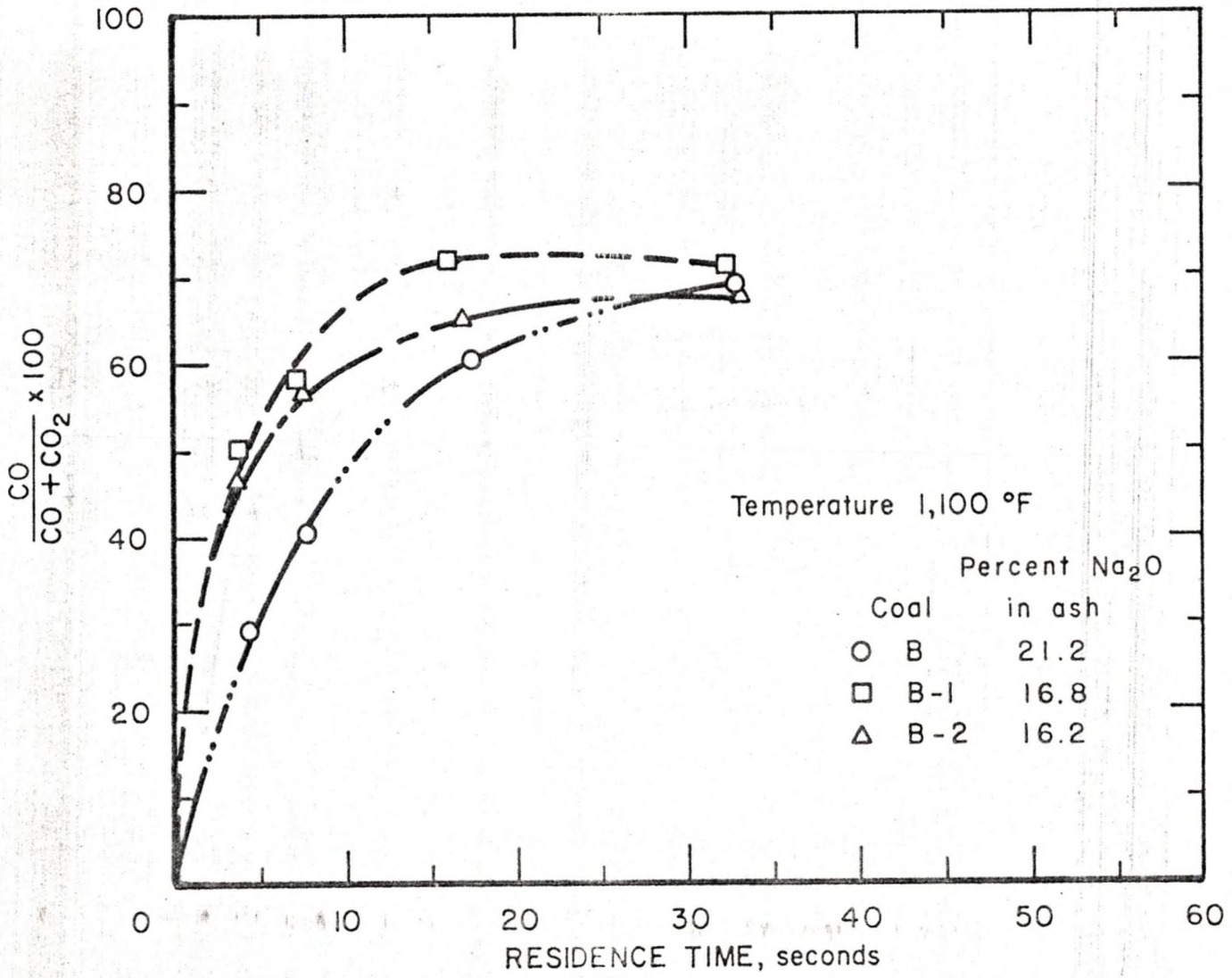

Fig. 9--Percent CO vs residence time, results of sodium tests for coal B at 1,100 °F.

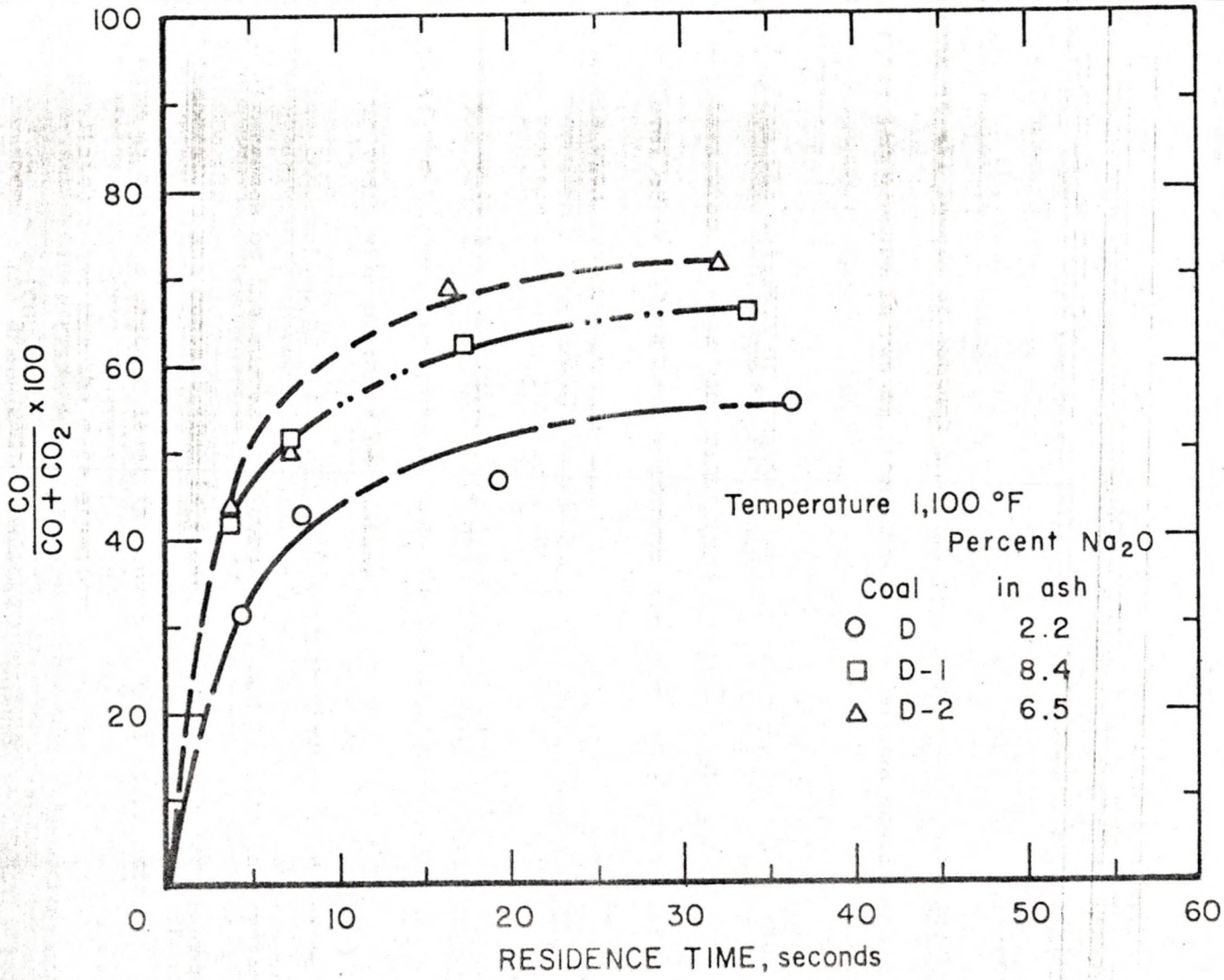

Fig. 10 -- Percent CO vs residence time, results of sodium tests for coal D at 1,100 °F.

DISCUSSION

Coal Rank

The rank of coal was found to have a definite effect on the conversion of CO_2 to CO, with the degree of conversion decreasing with increasing rank at all levels of contact time and temperature tested. However, as the temperature increases, the differences between coals become smaller.

From the analysis of variance data in Table 9, it can be seen that the interaction effects were significant. Significant interactions mean that level of variables tested effects response. The interaction of coals with temperature are illustrated in Figures 6, 7 and 8. As the temperature level increased the curves become closer together. This is due to the temperature dependence of the reaction and indicates that if the temperature level is high enough the conversions for the four coals will probably be similar.

The interaction of the coals with contact time is illustrated by the divergence of the curves in Figures 6, 7 and 8. The interaction of temperature and contact time is shown by the way the curves become steeper as the temperature level increases. These interactions are predictable because the rate equation

$$r_{CO} = k_1(CO_2) - k_2(CO)^2$$

shows the dependence of the conversion on time and the rate constants k_1 and k_2. The rate constants are in turn dependent on the carbon source and the temperature.

Thermodynamic Data

The heats of reaction at 298° K, ΔH°_{298}, were calculated from the pseudo-equilibrium constants at 1400° F. The heats of formation, ΔH°_{f}, of the carbon in the coals relative to the heat of formation of beta graphite were also calculated. The heat of formation of beta graphite is taken to be zero by convention and the ΔH°_{298} for the reaction is 41,224 calorie per gram mole. The values of ΔH°_{298} of the reaction of the coals were found to be 44,057 calories per gram mole for coal A, 37,215 calories per gram mole for coal B, 40,800 calories per gram mole for coal C, and 38,994 calories per gram mole for coal D. It is evident that the heats of reaction for the lignite and subbituminous coals are less than those of beta graphite and the bituminous coal. In effect, this means that the reactions of the low rank coals are less endothermic than that of the bituminous coal.

The heats of formation calculated for the carbon in the coals were 2833 calories per gram mole for coal A, -4009 calories per gram mole for coal B, -424 calories per gram mole for coal C and -2230 calories per gram mole for coal D. This shows the carbon in the lignite and subbituminous coals to be in a lower state with regard to enthalpy than the bituminous coal or the reference carbon, beta graphite, if the pseudo equilibrium values can be considered to represent equilibrium. It had previously been established that the carbon in cokes can differ in reactivity with beta graphite by as much as 2600 calories.

The reasons for the differences in conversion due to the coals and the differences in the heats of reaction probably stem from two sources, the structure of the coals and their mineral matter content.

Coal Structure

Coal is formed from plant debris, which, under the influence of pressure, temperature and time, becomes coalified through the processes of dehydration, demethanation and decarboxylation. As the coalification process advances, the coal becomes more aromatic in character as straight chain carbon groups, peripheral groups such as carboxyl, methyl and the cross linking straight chain groups are eliminated. In terms of structure this means that the coal becomes a more tightly knit unit as coalification proceeds.

In the lignites, the lowest rank of coal, the coalification process is not as far advanced as in the subbituminous and bituminous coals. As a consequence of this, the lignites are not as condensed in structure and are more porous than the higher rank coals. Because of the greater porosity, the lignites exhibit greater surface area. The internal pore surface of lignites can range as high as 180 square meters per gram while the internal surface of bituminous coals can be as low as 40 square meters per gram with the subbituminous coals falling in between (12). The greater surface area of the lignite coals means a greater number of possible sites for the reaction between CO_2 and the coal substance. This may be part of the reason for the greater conversion of CO_2 by the lignites.

Another reason for the differences in conversion may be the degree of aromaticity. Higher aromatic compounds have a lower average bond order and a lower average free valance than do the simpler aromatics.

It is known that substitution reactions preferably take place at bonds where the free valance is maximum while addition reactions take place more readily at bonds with a high bond order (12). The mechanism of the Bouduard reaction is not positively known, but if it is substitution or addition, the reaction should result in greater conversion for coals of low aromatic character. The higher conversion for the lignites of lower aromatic character than the bituminous coal supports this conclusion.

Mineral Content

Most of the coals in the United States average from 6 to 10 percent ash. The character and amount of the ash varies with the location and rank of the coals. Because of the soil conditions in North Dakota, the lignite coals found there have a high content of the alkaline metals, sodium and calcium. At present there is evidence to predict that sodium and calcium positively affect gasification (6).

This investigation also revealed evidence as to the effect of sodium on the reactivity of coals with CO_2. The samples of char to which sodium had been added produced more CO than under similar conditions the original sample and the chars from the two lignites which. differ in sodium content were found to differ in reactivity.

Char from coal B with 21 percent sodium as sodium oxide in its ash was found to be more reactive than char from coal D with 2 percent sodium oxide in its ash. Both of these samples were derived from lignites so the effects of rank are considered equal. The difference is then attributed to the mineral constituents, especially sodium, in their ash.

Samples of char from coal D to which sodium was added were found to be more reactive than the original char. These results follow more closely the results of previous investigations than do the results of the tests made with samples of char from coal B from which sodium had been leached. The leached samples of char from coal D which had lower sodium contents were found to be somewhat more reactive. It is possible, however, that the treatment of these samples with the strong acid solutions may have changed the physical state of the samples.

Because of the small number of experiments performed, it is not possible to predict a definite trend in the relationship of reactivity and the sodium content of the source coals. Future work should be carried out using a greater number of tests at different sodium levels in an effort to make a definite correlation between the reactivity of coals and sodium content. Such further investigations should also include the determination of the effects of other alkaline metals on reactivity.

The determination of the effects of the ash constituents would be of great value in forming a set of criteria for selecting or preparing coals for gasification.

Advantages of Gasifying Low Rank Coals

There are two important advantages in using the lower rank coals in gasification. The first is the greater reactivity of the low rank coals and the second is their abundance.

It has been shown that the reaction of the low rank coals is less endothermic than that of the bituminous coal and that high conversions of CO_2 can be attained at relatively low temperatures. Operation at low temperatures is advantageous because it requires a lower expenditure of energy to carry out the reaction. Lower temperatures also result in a reduction of the heat losses to the surroundings which means an increase in thermal efficiency.

In addition to being well suited for several gasification processes, the low rank coals may prove to be useful in underground gasification. Gasification of coal "in situ" can be greatly benefitted if significant conversion can be attained at low temperatures. There is no sure way to control the temperature of underground gasification, consequently in some situations losses to the surroundings result in low temperatures.

Low rank coals may possibly be gasified underground using an air or oxygen-enriched air blast to produce a gas rich in CO which could be purified and reformed to a mixture of CO and hydrogen by the water gas shift reaction. Preparation of a synthesis gas in this manner is not presently economically feasible, but may be in the future (13).

Abundance of Low Rank Coals

The question of the feasibility of the use of low rank coals for gasification would be entirely academic if there were few deposits of these coals. However, it is estimated that the lignite and subbituminous coals make up 45 percent of the United State's coal reserves (1). The combined tonnages of these coals has been estimated at 876 billion tons of which there are 350 billion tons of lignite in North Dakota (14).

Of the lignite in North Dakota, about 10 percent is readily mined by strip mining.

Because of their abundance and mineability, these coals are a low cost source of raw materials. The reserves of lignite and subbituminous coals are as yet relatively untapped. The reasons for this are the unsuitability of these coals for the production of metallurgical coke and the remoteness of the deposits in relation to industry and population centers. The remoteness, low heating value and high moisture content have restricted the use of these coals for electrical power generation because of the high cost of transportation. The exceptions to this are the cases in which the coals are utilized near the mine or where environmental concern over sulfur dioxide pollution makes long distance shipping necessary.

While shipping the lignites and subbituminous coals long distances is economically unfeasible, the pipelining of a synthetic gas is not. Gasification and pipeline transport will be an important means of moving the stored energy in coal to points of need.

CONCLUSIONS

The results of the experiments performed and observations support the following conclusions:

1. Coals of different rank differ in reactivity with CO_2 in forming CO.

2. As the rank of the coals increases, the reactivity in terms of conversion of CO_2 decreases.

3. Low-rank coals may be well suited for the manufacture of a synthetic gas for production of a high-heating-value pipeline gas.

4. The reactivity of a coal can be altered by modifying the sodium content of the coal.

5. Temperature and space time also have significant effects on the conversion of CO_2 to CO by the Bouduard reaction.

6. Severe treating of the chars, such as acid leaching, may affect the reactivity.

RECOMMENDATIONS FOR FUTURE WORK

The investigations in this study are not complete. The following recommendations are suggested for future work:

1. The variables of coal rank and sodium concentration should be separated into individual investigations, each of which could be carried out in greater depth.

2. The reactivity experiment should be revised so that the test material is the only variable from one test to another. An example of such a test is the Muller-Jandl reactivity test for coke (15).

3. To determine the relationship of sodium concentration to reactivity, a greater number of samples should be prepared and tested.

4. The effect of sodium on the reactivity of high-rank coals, such as bituminous coals, should be determined.

APPENDIX A

TABLE 1

COALS TESTED

Coal	Mine	Town	County	State	Operator
A	Arkwright	Osage	Monangalia	W. Va.	Consolidation Coal Co.
B	Larson Pit	Larson	Burke	N. Dak.	Baukol-Noonan, Inc.
C	Colstrip	Colstrip	Rosebud	Montana	Western Energy Co.
D	Gascoyne	Gascoyne	Bowman	N. Dak.	Knife River Coal Mining Co.

TABLE 2

ANALYSES OF COALS AS RECEIVED

Proximate Analysis				
Coal	A	B	C	D
Percent moisture	1.1	24.6	19.0	34.9
Percent volatile matter	37.8	30.5	32.1	27.9
Percent fixed carbon	54.2	32.7	41.0	25.6
Percent ash	6.8	7.2	7.9	9.6
Elemental Analysis				
Coal	A	B	C	D
H_2	5.3	6.0	5.9	6.6
C	77.3	50.1	54.9	39.9
N_2	1.6	0.8	0.8	0.6
O_2	6.8	35.5	29.8	42.3
S	2.1	0.3	0.7	1.0
Ash	6.8	7.2	7.9	9.6

TABLE 3

ASH ANALYSES OF CHARS

Coal	A	B	C	D
Loss on ignition at 800° C	0.3	1.2	0.3	0.2
Silica, SiO_2	45.8	18.8	35.6	29.2
Aluminum oxide, Al_2O_3	28.0	12.0	19.7	11.7
Ferric Oxide, Fe_2O_3	17.7	7.2	7.3	7.4
Titanium oxide, TiO_2	0.8	0.2	0.7	0.5
Phosphorous pentoxide, P_2O_5	0.3	0.3	0.3	0.1
Calcium oxide, CaO	2.5	14.8	14.5	18.1
Magnesium oxide, MgO	1.2	3.2	4.6	6.6
Sodium oxide, Na_2O	0.8	21.2	0.2	2.2
Potassium oxide, K_2O	0.8	0.3	0.1	0.3
Sulfur trioxide, SO_3	2.6	17.5	15.8	22.7

TABLE 4

PROXIMATE ANALYSES OF CHARS

Coal	H_2O, as rec'd	Volatile matter, as rec'd	Fixed carbon, as rec'd	Ash, as rec'd
A	0.6	19.6	71.4	8.4
B	2.1	24.2	61.9	11.9
C	1.5	27.0	60.2	11.2
D	8.7	32.1	45.7	13.6

TABLE 5

ASH ANALYSES OF CHAR SAMPLES PREPARED FROM COAL B

Coal	B	B-1	B-2
Loss on ignition at 800° C	1.2	1.2	1.7
Silica, SiO_2	18.8	25.0	20.8
Aluminum oxide, Al_2O_3	12.0	15.9	14.0
Ferric oxide, Fe_2O_3	7.2	6.0	6.1
Titanium oxide, TiO_2	0.2	0.4	0.2
Phosphorus pentoxide, P_2O_5	0.3	0.1	0.0
Calcium oxide, CaO	14.8	15.3	24.8
Magnesium oxide, MgO	3.2	3.6	3.4
Sodium oxide, Na_2O	21.2	16.8	16.2
Potassium oxide, K_2O	0.3	0.3	0.5
Sulfur trioxide, SO_3	17.5	13.3	10.9
Total	96.7	97.9	98.6

TABLE 6

ASH ANALYSES OF CHAR SAMPLES PREPARED FROM COAL D

Coal	D	D-1	D-2
Loss on ignition at 800° C	0.2	0.3	0.2
Silica, SiO_2	29.2	22.7	23.2
Aluminum oxide, Al_2O_3	11.7	10.9	11.0
Ferric oxide, Fe_2O_3	7.4	6.2	6.5
Titanium oxide, TiO_2	0.5	0.6	0.7
Phosphorus pentoxide, P_2O_5	0.1	0.1	0.1
Calcium oxide, CaO	18.1	20.9	20.9
Magnesium oxide, MgO	6.6	8.0	8.0
Sodium oxide, Na_2O	2.2	8.4	6.5
Potassium oxide, K_2O	0.3	0.3	0.3
Sulfur trioxide, SO_3	22.7	22.1	23.4
Total	99.0	100.5	100.8

TABLE 7

WEIGHT OF SAMPLES CHARGED, GRAMS

	1100° F	1250° F	1400° F
Char A	204	201	206
Char B	267	269	267
Char C	256	261	261
Char D	251	249	249
Char B_1	275	---	---
Char B_2	281	---	---
Char D_1	247	---	---
Char D_2	253	---	---

APPENDIX B

TABLE 8

TEST RESULTS[a]

Temperature	Space time, seconds	Coal			
		A	B	C	D
1100° F	5	1.9	29.6	24.0	31.4
	10	4.4	40.6	27.7	42.9
	25	15.7	60.6	27.0	46.4
	50	27.1	69.0	36.3	55.1
1250° F	5	10.0	78.4	49.9	60.4
	10	18.2	87.8	57.0	69.4
	25	34.4	92.6	66.5	77.0
	50	44.0	92.5	71.3	79.8
1400° F	5	30.0	97.0	80.6	91.5
	10	42.1	98.2	85.4	93.8
	25	56.5	97.8	94.3	95.2
	50	67.1	98.0	94.6	95.4

[a]Results reported as $\frac{CO}{CO + CO_2} \times 100$

TABLE 9

ANALYSIS OF VARIANCE FOR 3 x 4 x 4 FACTORIAL

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F	Critical F	Estimated mean square
Temperature (A)	19058.9	2	9529.4	726.9	$F_{0.05(2,18)} = 3.55$	$s^2 + 3s^2_{ab} + 16s^2_a$
Coal (B)	16580.1	3	5526.7	421.6	$F_{0.05(3,18)} = 3.16$	$s^2 + s^2_{abc} + 4s^2_{ab} + 3s^2_{bc} + 4b^2$
Space time (C)	2902.9	3	967.63	73.8	$F_{0.05(3,18)} = 3.16$	$s^2 + 4s^2_{ac} + 12s^2_c$
A x B	994.1	6	165.7	12.6	$F_{0.05(6,18)} = 2.66$	$s^2 + s^2_{abc} + 4s^2_{ab}$
A x C	286.9	6	47.8	3.6	$F_{0.05(6,18)} = 2.66$	$s^2 + 4s^2_{ac}$
B x C	614.7	9	68.3	5.2	$F_{0.05(9,18)} = 2.46$	$s^2 + s^2_{abc} + 3s^2_{bc}$
Subtotal	40437.6	29				
Error	236.1	18	13.11			$s^2 + s^2_{abc}$
Total	40673.7	47				

TABLE 10

EQUILIBRIUM CONSTANTS FOR BETA GRAPHITE

T	ln K	K
1100° F	-1.911	0.147
1250° F	0.449	1.3
1400° F	2.45	8.12

TABLE 11

CALCULATED K_p's BASED ON ACTUAL PERCENTAGES OF CO AND CO_2

Temp.	Coal A	Coal B	Coal C	Coal D
1100° F	0.087	1.54	0.192	0.548
1250° F	.336	10.37	1.67	3.01
1400° F	1.29	43.6	15.57	15.73

TABLE 12

SODIUM TEST RESULTS FOR COAL B[a]

Space time, seconds	Coal		
	B	B-1	B-2
5	29.6	46.5	50.1
10	40.6	57.6	58.2
25	60.6	65.1	72.0
50	69.0	68.7	71.0

[a]Results reported as $\frac{CO}{CO + CO_2} \times 100$

TABLE 13

SODIUM TEST RESULTS FOR COAL D[a]

Space time, seconds	Coal		
	D	D-1	D-2
5	31.4	42.0	43.4
10	42.9	51.3	50.5
25	46.4	62.0	68.5
50	55.1	65.4	71.3

[a]Results reported as $\frac{CO}{CO + CO_2} \times 100$

TABLE 14

ANALYSIS OF VARIANCE FOR TWO WAY CLASSIFICATION OF EFFECTS OF SODIUM CONCENTRATION AND SPACE TIME FOR COAL D

Source of variation	Sums of squares	Degrees of freedom	Mean squares	Calculated F	Critical F	Estimated mean squares
Sodium concentration	562.5	2	281.25	42.54	$F_{0.05(2,6)} = 5.14$	$s^2 + 4s_a^2$
Space time	1127.0	3	375.66	56.83	$F_{0.05(3,6)} = 4.76$	$s^2 + 3s_b^2$
Error	37.7	6	6.61			s^2
Total	1649.8	11				

TABLE 15

ANALYSIS OF VARIANCE FOR TWO WAY CLASSIFICATION OF EFFECTS OF SODIUM CONCENTRATION AND SPACE TIME FOR COAL B

Source of variation	Sums of squares	Degrees of freedom	Mean squares	Calculated F	Critical F	Estimated mean squares
Sodium concentration	356.9	2	178.45	7.06	$F_{0.05(2,6)} = 5.14$	$s^2 + 4s_a^2$
Space time	1449.4	3	483.13	19.13	$F_{0.05(3,6)} = 4.76$	$s^2 + 3s_b^2$
Error	151.5	6	25.25			s^2
Total	1957.8	11				

APPENDIX C

CALCULATIONS

Calculations made included the computation of the flow rates necessary to provide the space times used, the calculation of the residence times, the calculations for the heats of reaction and equilibrium constants of the carbon and the analysis of variance calculations.

Flow Rate Calculation

The space times used were determined by the flow rate of the gases through the bed of char. The space time was defined as the void volume of the bed divided by the volume flow rate CO_2 through the bed.

The volume of the bed is equal to the product of the cross sectional area of the bed and its depth. The bed depth, 30.0 centimeters, provided a volume of:

Volume = 30.0 cm x 13.3 cm^2 = 400 cm^3

The void volume of the bed was calculated by multiplying the bed volume by an assumed fraction of voids in the bed. The void fraction was assumed to be 0.45 for a bed of particles of the size range used (5).

Void volume = 0.45 x 400 cm^3 = 180 cm^3

The flow rate necessary to produce a space time of 5 seconds in a 400 cubic centimeters bed with a void volume of 180 cubic centimeters is calculated as follows:

$$\text{Space time} = \frac{\text{void volume}}{\text{volume flow rate}}$$

$$\text{Volume flow rate} = \frac{180 \text{ cm}^3}{5 \text{ sec}} = 36.0 \text{ cm}^3/\text{sec}$$

This is the required volume flow rate at the temperature of the reactor and it must be corrected to the temperature at which the flow will be metered. This is done as follows:

$$\text{Flow rate at } 70^\circ \text{ F} = 36.0 \text{ cm}^3/\text{sec} \times \frac{(460 + 70)^\circ\text{R}}{(460 + 1100)^\circ\text{R}} = 12.3 \frac{\text{cm}^3}{\text{sec}}$$

Flow rates were calculated for space times of 5, 10, 25 and 50 seconds at temperatures of 1100° F, 1250° F and 1400° F. Corrections for pressure were not necessary as the reaction was carried out essentially at atmospheric pressure.

The choice of 30.0 centimeters as the bed depth was arbitrary, but calculations using 30.0 centimeters as the bed depth showed that carbon usage would not exceed the 20 to 50 percent under conditions of maximum reaction. Wenzel, Meraikib and Franke (6) have found that carbon depletion in this range should not affect the reactivity determination. The weights of the reacted samples showed that these estimates were essentially correct.

Residence Time Calculation

The space times are sufficient for designating the feed rates used in the experiments, but are not indicative as to what happens due to the increase in volume of the gases. The space times are

too high when the conversion of CO_2 to CO is considered. To give a better picture of what was happening the plots in Figures 6, 7, 8, 9 and 10 were drawn for the percentage of CO versus the residence time based on flow leaving the reactor. Since this quantity was not measured, it was necessary to calculate the flow rate from the conversion.

Let:

V_1 = volume flow rate into reactor,

V_2 = volume flow rate from reactor,

X = percent CO,

and Z = conversion of CO_2 to CO.

From the equation of the Bouduard reaction,

	$CO_2 + C$	$2CO$
before reaction	1	0
after reaction	1 - Z	2Z

We can see that the total volume leaving the reactor will be:

$$V_2 = V_1 (1 - Z + 2Z)$$

$$V_2 = (1 + Z) V_1$$

The presence of CO_2 in the exit gas is:

$$X = \frac{2Z \times V_1}{(2Z \times V_1) + [(1-X) V_1]}$$

or

$$X = \frac{2Z}{1 + Z}$$

Since the experimental data provides the percent CO it is possible to calculate the conversion, Z.

$$Z = \frac{X}{2-X}$$

It is now possible to calculate the flow rate of gas from the reactor from the flow rate of CO_2 into the reactor and the percent CO in the exit gas. The residence time is equal to the space time multiplied by the ratio of V_1 over V_2.

Analysis of Variance Calculations

An example of the analysis of variance for the data in Table 6 is shown below:

$$\Sigma X = 539.7$$

$$\Sigma X^2 = 23{,}367.3$$

$$\frac{(\Sigma X)^2}{N} = \frac{(539.7)^2}{16} = 18{,}204.7$$

$$\frac{\Sigma (\text{Column totals})^2}{c} = 21{,}012.7$$

$$\frac{\Sigma (\text{row totals})^2}{r} = 19{,}620.3$$

$$\text{sum of squares (coals)} = \frac{\Sigma (\text{column totals})^2}{c} - \frac{(\Sigma X)^2}{N} = 2808.0$$

$$\text{sum of squares (contact times)} = \frac{\Sigma (\text{row totals})^2}{r} - \frac{(\Sigma X)^2}{N}$$

$$= 1415.6$$

$$\text{sum of squares (total)} = \Sigma (X)^2 - \frac{(\Sigma X)^2}{N}$$

$$= 23{,}367.3$$

$$\text{sum of squares (error)} = SS(\text{total}) - SS(\text{coals}) - SS(\text{contact times})$$

$$= 939.0$$

The degrees of freedom for the coals and the contact times are the number of coals minus one and the number of contact times minus one. The total number of degrees of freedom is the number of elements in the table minus one. The number of error degrees of freedom is the total degrees of freedom minus the degrees of freedom for coals and contact times.

The mean squares are calculated by dividing each sum of squares with the corresponding number of degrees of freedom. The F tests are made by dividing the mean squares of the effects by the mean square of the error term. The results of the F tests are then compared with the critical F value to determine significance. The ANOVA tables prepared from these calculations are shown in Appendix B, Tables 9, 14 and 15.

Equilibrium Constants for Beta Graphite

The equilibrium constants were calculated from published data for the free energies, F, heats of formation, ΔH_f, and heat capacities of CO, CO_2 and beta graphite.

The relationship of the equilibrium constant, K, with temperature is:

$$\ln K = \frac{\Delta H_o}{RT} + \frac{a}{R} \ln T + \frac{b}{2R} T + \frac{c}{6R} T^2 + C \qquad (16).$$

To use this relationship it is necessary to solve for the constant c. This is done in the following manner:

$$\ln K = \frac{-\Delta F}{RT}$$

at 298° K

$$\Delta F^o(\text{reaction}) = 2\,(\Delta F^o_{CO}) - \Delta F^o_{CO_2}$$

$$\Delta F^o = 2\,(-32808) - (-94260)$$

$$= 28644 \text{ cal/gm mole}$$

$$\ln K = \frac{-28644 \text{ cal/gm mole}}{(1.987 \text{ cal/gm mole } ^\circ K)\ (298^\circ K)}$$

$$= -48.3$$

$$\Delta H^\circ_{298} = 2\ (\Delta H^\circ_{f\text{-}CO}) - \Delta H^\circ_{f\text{-}CO_2}$$

$$= 2\ (-26416) - (-94052)$$

$$= 41220 \text{ cal/gm mole}$$

$$\Delta H_o = \Delta H_{298} - aT - \frac{b}{2} T^2 - \frac{c}{3} T^3 \qquad (16).$$

$$a = 2\ (6.42) - 6.214 = 6.626$$

$$b = [2\ (1.164) - 10.396] \times 10^{-3} = -8.066 \times 10^{-3}$$

$$c = [2\ (-.196) = 3.545] \times 10^{-6} = 3.153 \times 10^{-6}$$

Using these values of a, b, and c, obtained from the heat capacities of the products and reactants, and letting $T = 298^\circ$, ΔH_o can be calculated. By substitution into the first equation, the constant, C, can be determined. The final equation for calculating K at any temperature is:

$$\ln K = \frac{\Delta H_o}{RT} + 3.33 \ln T - 2.03 \times 10^{-3} T + 2.64 \times 10^{-7} T^2 + 3.031$$

$$+ 2.64 \times 10^{-7} T^2 + 3.031.$$

Calculation of K_p

The equilibrium constant, K_p, is calculated from the equilibrium partial pressures of the components in the gas mixture as follows:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(P_t\ Y_{CO})^2}{P_t\ Y_{CO_2}} \qquad (16).$$

In the experiment performed, P_t was equal to one atmosphere so:

$$K_p = \frac{(Y_{CO})^2}{Y_{CO_2}}$$

where Y_{CO} is the mole fraction or volume percent of the gas. For calculating the values of K_p, the original data for percents CO and CO_2 were used.

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